is the fraction of complexed solute, the equilibrium constant is given by

$$K = \frac{f}{1-f} = \exp\left(\frac{-\Delta H^\circ}{RT}\right)\exp\left(\frac{\Delta S^\circ}{R}\right)$$

The value of $f$ at any temperature is taken equal to $(\delta_t - \delta_0)/(\delta_c - \delta_0)$ where $\delta_t$ and $\delta_c$ are the observed chemical shifts at temperature $t$ and the proton resonance frequency in the pure complex at 0°K, respectively; the proton chemical shift in an "inert" solvent such as carbon tetrachloride is taken to give $\delta_0$. From the slope of a plot of log $K$ against $1/T$, the enthalpy of complex formation can be estimated. To calculate these thermodynamic parameters, we have used the temperature-dependent ring proton frequencies ($\delta_t$) of [pip][Y(tfac)$_4$] in the equilibrium mixture (Figure 5) to get $\delta_c$ ($-6.06$ ppm); $\delta_0$ was taken as $-5.57$ ppm, the chemical shift of [pip][Y(tfac)$_4$] –CH= resonance in carbon tetrachloride. The intercept and the slope of the log $K$ *vs.* $1/T$ plot produced an entropy of formation of $-12.9 \pm 2.5$ eu and an enthalpy of formation of $-2.5 \pm 0.6$ kcal/mol, a value similar to the value of $-2.7 \pm 0.5$ kcal/mol reported for a 1:1 complex between chloroform and acetone,[38] in which complex formation occurs *via* hydrogen bonding between the $CHCl_3$ proton and the carbonyl oxygen of acetone. It is tempting to suggest that hydrogen bonding occurs between $CDCl_3$ deuterium and the carbonyl oxygen atoms of the β-diketonate ligand in these metal-diketonate complexes.[39,40] However, the values of entropy and enthalpy of formation should be taken with caution in view of the assumptions[37] for and the criticisms[41] of this model.

**Acknowledgment.**—The support of this research by the National Research Council of Canada through Grant No. A-5443 is gratefully acknowledged. We also thank Professor R. C. Fay for helpful discussions.

[38] R. Kaiser, *Can. J. Chem.*, **41**, 430 (1963).

[39] N. Serpone, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1968.

[40] Studies are being carried out in this laboratory to elucidate further whether hydrogen bonding occurs between the $CHCl_3$ proton and the carbonyl oxygens or between the $CHCl_3$ proton and the π electrons of the β-diketonate ring. Previous studies have not been conclusive as to the site of hydrogen bonding [*cf.* T. S. Davis and J. P. Fackler, Jr., *Inorg. Chem.*, **5**, 242 (1966)].

[41] P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 231 (1967).

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# The Syntheses and Properties of β,β′,β′′-Triaminotriethylamine Chelates of the Tripositive Lanthanide Ions

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The reaction of β,β′,β′′-triaminotriethylamine with a lanthanide(III) nitrate salt in anhydrous acetonitrile yields solid compounds of the type [Ln(tren)$_2$](NO$_3$)$_3$, [Ln(tren)$_2$NO$_3$](NO$_3$), and [Ln(tren)(NO$_3$)$_3$]. Nitrate ion coordination in several of the complexes is established by infrared data. Conductivity data indicate that [Ln(tren)(NO$_3$)$_3$] is the thermodynamically favored species in acetonitrile solutions containing the nitrate salts. However, nmr data establish Ln(tren)$_2^{3+}$ as the stable species in solutions containing the perchlorate salts. The enthalpy changes observed upon complexation of the lanthanide perchlorate salts in acetonitrile establish tetradentate coordination by the amine.

## Introduction

High-coordinate lanthanide complexes derived from the strongly basic nitrogen donors ethylenediamine,[2] 1,2-propanediamine,[3] and diethylenetriamine[4] were isolated recently utilizing a nonaqueous solvent as the reaction medium. These species are rapidly hydrolyzed and must be handled under anhydrous conditions. Of special significance is the observation that these cationic complexes are enthalpy stabilized and possess considerable thermodynamic stability in acetonitrile.[4,5]

Coordination numbers of 6 through 12 have been observed in lanthanide complexes.[6,7] That such a wide variation occurs may be attributed to steric factors and electrostatic forces of attraction and repulsion, rather than bond orientation by the well-shielded 4f orbitals of the metal ion. Thus the large size of the lanthanide ions allows coordination of four bidentate ethylenediamine or 1,2-propanediamine molecules and three tridentate diethylenetriamine molecules. In the latter example, increased steric crowding was observed in the tris chelates with decreasing metal ion radius. Additional anion coordination was established in the tetrakis-ethylenediamine and -propanediamine chelates and was found to be dependent upon both anion size and metal ion size.

We report here the syntheses of the first lanthanide complexes derived from the tetradentate N donor β,β′,β′′-triaminotriethylamine (tren) isolated as mono and bis chelates of the nitrate salts. The total coordination number in these species and its variation across the lanthanide series were determined by elemental analysis and infrared spectroscopy. Further characterization in solution was accomplished utilizing conductivity mea-

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[1] (a) St. Louis University. (b) Arizona State University.

[2] (a) J. H. Forsberg and T. Moeller, *Inorg. Chem.*, **8**, 883 (1969); (b) J. H. Forsberg and T. Moeller, *J. Amer. Chem. Soc.*, **90**, 1932 (1968).

[3] L. J. Charpentier and T. Moeller, *J. Inorg. Nucl. Chem.*, **32**, 3575 (1970).

[4] J. H. Forsberg and C. A. Wathen, *Inorg. Chem.*, **10**, 1379 (1971).

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[6] T. Moeller, E. R. Birnbaum, J. H. Forsberg, and R. B. Gayhart, *Progr. Sci. Technol., Rare Earths*, **3**, 66 (1968).

[7] T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965).

surements and nmr spectroscopy. Calorimetric measurements of enthalpies of complexation of lanthanide perchlorates in acetonitrile were obtained in order to establish tetradentate coordination by the ligand.

## Experimental Section

**Materials.**—The lanthanide oxides, all of 99.9% purity, were obtained from American Potash and Chemical Corp. The anhydrous lanthanide salts were prepared by the general procedures described previously.[2a] Reagent grade acetonitrile was dried and purified by distillation from phosphorus(V) oxide. Triaminotriethylamine was extracted from technical grade triethylenetetramine (Fisher Scientific).

**Conductivity Measurements.**—Conductivities were determined with an Industrial Instruments Inc. Model RC 16B2 conductance bridge at 1000 cps in a constant-temperature mineral oil bath maintained at 25 ± 0.01°. The constant-temperature bath was contained in a drybag.

**Spectra.**—The $^1$H nmr spectra were obtained on a Varian HA-100 spectrometer at ambient temperature. Infrared spectra in the region 4000–650 cm$^{-1}$ were obtained with a Perkin-Elmer Model 457 grating instrument as Nujol and hexachlorobutadiene mulls supported between sodium chloride plates. Polystyrene film was used to calibrate the instrument.

**Enthalpy Measurements.**—The calorimeter used in this study has been described previously.[4,5] A 1-mmol quantity of tren was dissolved in 125 ml of acetonitrile contained in the dewar. The solution was maintained slightly below ambient at 23° and controlled within ±0.2° during each experiment. Lanthanide perchlorates were added as acetonitrile solutions (0.200 ml of 0.2 *M* $Ln(ClO_4)_3$) using a 2-ml Gilmont micrometer syringe. The enthalpies of complexation were corrected for the heat of dilution observed upon addition of the metal ion solution. Approximately ten enthalpy measurements were made in each run and the values were averaged to obtain the molar enthalpy of complexation.

**Analyses.**—Elemental carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc. Lanthanide analyses were performed in this laboratory by titration with ethylenediaminetetraacetic acid, using xylenol orange as the indicator.

**Preparation of $\beta,\beta',\beta''$-Triaminotriethylamine.**—$\beta,\beta',\beta''$-Triaminotriethylamine was extracted from technical grade triethylenetetramine by fractional precipitation of the hydrochloride salt (tren·3HCl).[8] Triethylenetetramine (200 g) was dissolved in 95% ethanol (750 ml) and cooled to 5° in an ice bath. Concentrated (12 *M*) hydrochloric acid was added dropwise from a buret at a rate such that the temperature of the reaction mixture was kept below 10°. A white, crystalline precipitate formed after the addition of 50 ml of acid. A chloride analysis of several fractions of the salt indicated that 105 ml of acid could be added before precipitating trien·4HCl. The tren·3HCl was recrystallized from a hot water–ethanol mixture and washed with ethanol, acetone, and diethyl ether. Approximately 3 l. of triethylenetetramine was needed to obtain 100 g of pure tren·3HCl.

The free amine was obtained from the hydrochloride salt by a reaction with a concentrated sodium hydroxide solution. Potassium carbonate was added to absorb water and salt the amine out of the aqueous solution. The solution was filtered, and the double-layered filtrate was collected in a separatory funnel. The amine was contained in the pale yellow, upper layer. The amine layer (*ca.* 80 ml) was vacuum distilled over potassium carbonate, giving a clear and colorless distillate (*ca.* 40 ml). The ligand was dried by a vacuum distillation over sodium at 135°. The purity of the final product was established by nmr.

**Synthesis of Complex Species.**—The complexes were prepared under anhydrous conditions by the direct reaction of $\beta,\beta',\beta''$-triaminotriethylamine with a lanthanide salt in acetonitrile. All manipulations were carried out in an inert-atmosphere box. The volume of solvent used is important, since the isolation of a stoichiometric product apparently depends upon the relative solubilities of the mono and bis chelates. The mono chelates were prepared by addition of 1 mmol of tren (neat) to a 5-ml solution containing 1 mmol of lanthanide nitrate. Although a precipitate forms immediately, the suspension was refluxed for 12 hr to ensure formation of a stoichiometric product. The products obtained without refluxing contain greater than a 1:1 ligand to metal ion mole ratio.

The bis chelates were prepared by a dropwise addition of 20 ml of 0.05 *M* $Ln(NO_3)_3$ solution to 15 ml of 0.20 *M* tren solution (ligand to metal ion mole ratio is 3:1). The resulting suspension was stirred for approximately 10 min. A stoichiometric bis chelate was obtained without refluxing. Products containing less than a 2:1 ligand to metal ion mole ratio were obtained when the total volume of solution was less than specified.

A complete list of complexes and their analyses are given in Table I. All products were hygroscopic, crystalline powders, which underwent rapid hydrolytic decomposition when exposed to the atmosphere.

TABLE I

COMPOUNDS PREPARED AND ANALYTICAL DATA

| | Analysis | | | | | |
|---|---|---|---|---|---|---|
| | % C | | % H | | % Ln | |
| Compound[a] | Calcd | Found | Calcd | Found | Calcd | Found |
| $[La(tren)_2NO_3](NO_3)_2$ | 23.32 | 23.06 | 5.83 | 6.02 | 22.50 | 22.57 |
| $[Pr(tren)_2NO_3](NO_3)_2$ | 23.25 | 23.04 | 5.81 | 6.01 | 22.80 | 22.75 |
| $[Nd(tren)_2NO_3](NO_3)_2$ | 23.12 | 23.00 | 5.78 | 5.94 | 23.16 | 23.20 |
| $[Sm(tren)_2](NO_3)_3$ | 22.90 | 22.19 | 5.72 | 6.46 | 23.91 | 23.91 |
| $[Eu(tren)_2](NO_3)_3$ | 22.86 | 22.93 | 5.70 | 5.84 | 24.10 | 24.10 |
| $[Gd(tren)_2](NO_3)_3$ | 22.65 | 22.35 | 5.66 | 5.76 | 24.74 | 24.90 |
| $[Dy(tren)_2](NO_3)_3$ | 22.50 | 22.36 | 5.63 | 5.73 | 25.35 | 24.76 |
| $[Er(tren)_2](NO_3)_3$ | 22.30 | 22.16 | 5.57 | 5.70 | 25.90 | 25.98 |
| $[Yb(tren)_2](NO_3)_3$ | 22.10 | 22.02 | 5.53 | 5.66 | 26.56 | 26.86 |
| $La(tren)(NO_3)_3$ | 15.28 | 15.19 | 3.82 | 3.83 | 29.48 | 29.67 |
| $Pr(tren)(NO_3)_3$ | 15.22 | 15.34 | 3.80 | 3.95 | 29.80 | 29.83 |
| $Nd(tren)(NO_3)_3$ | 15.11 | 15.15 | 3.78 | 3.82 | 30.27 | 30.43 |
| $Sm(tren)(NO_3)_3$ | 14.92 | 15.50 | 3.73 | 3.98 | 31.15 | 30.90 |
| $Gd(tren)(NO_3)_3$ | 14.71 | 14.79 | 3.68 | 3.71 | 32.13 | 32.13 |
| $Dy(tren)(NO_3)_3$ | 14.58 | 14.31 | 3.65 | 3.87 | 32.85 | 33.09 |
| $Er(tren)(NO_3)_3$ | 14.41 | 14.53 | 3.60 | 3.81 | 33.49 | 33.58 |
| $Yb(tren)(NO_3)_3$ | 14.25 | 14.48 | 3.56 | 3.73 | 34.25 | 34.06 |

[a] Coordination sphere dictated by infrared data.

## Results and Discussion

**Infrared Studies.**—The infrared spectra of mono- and bis-tren complexes of the lanthanide nitrates, in the regions of nitrate absorptions, are depicted in Figure 1. Assignments of the nitrate absorptions, based upon the two possible symmetry types, $D_{3h}$ (free nitrate) and $C_{2v}$ (coordinated nitrate), are presented

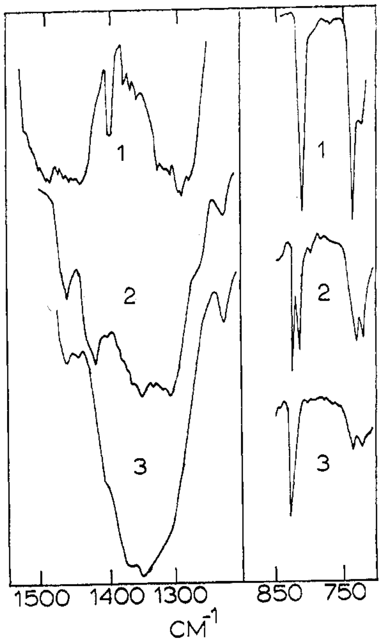

Figure 1.—Infrared spectra of $Ln(tren)_n(NO_3)_3$ species in the regions of nitrate absorptions: 1, $Ln(tren)(NO_3)_3$, Ln = La, Pr, Nd, Sm, Gd, Dy, Er, Yb; 2, $[Ln(tren)_2NO_3](NO_3)_2$, Ln = La, Pr, Nd; 3, $[Ln(tren)_2](NO_3)_3$, Ln = Sm, Eu, Gd, Dy, Er, Yb.

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(8) L. J. Wilson and N. J. Rose, *J. Amer. Chem. Soc.*, **90**, 6041 (1968).

TABLE II

ASSIGNMENT OF BANDS IN REGIONS OF NITRATE ABSORPTIONS (CM$^{-1}$)[a]

| Assignment | [Ln(tren)X$_3$] | [Ln-(tren)$_2$X]X$_2$ | [Ln(tren)$_2$]X$_3$ |
|---|---|---|---|
| $\nu_2(D_{3h}$ NO$_3)$ | ... | 1350 | 1350 |
| $\nu_3(D_{3h}$ NO$_3)$ | ... | 832 | 832 |
| $\nu_2(C_{2v}$ NO$_3)$ | 1310 | 1305 | ... |
| $\nu_3(C_{2v}$ NO$_3)$ | 740 | ... | ... |
| $\nu_4(C_{2v}$ NO$_3)$ | 1470 | 1420 | ... |
| $\nu_6(C_{2v}$ NO$_3)$ | 819 | 820 | ... |
| $\delta(CH_2)$ | ... | 1460 | 1465 |
| $\omega(CH_2)$ | 1400, 1375, 1365, 1358 | 1400 | 1405 sh |
| $\gamma(CH_2)$ | 1296 | ... | 1296 sh |
| $\omega(NH_2)$ | ... | 1325 | ... |

[a] $X^- = NO_3^-$.

in Table II.[9,10] The ligand absorptions in this region were identified in the spectrum of the mono and bis chelates of ErCl$_3$ and are assigned in Table II. The identification of the $\nu_2(C_{2v})$ absorption of the nitrate group was not possible due to strong absorptions by the ligand in the 1030-cm$^{-1}$ region.

The data indicate that all of the mono chelates may contain only coordinated nitrate groups, suggesting the formulation [Ln(tren)(NO$_3$)$_3$] (Table I). This formulation is analogous to that established for the bis-ethylenediamine chelate of neodymium nitrate, [Nd(en)$_2$(NO$_3$)$_3$].[1] A distinction between bidentate and monodentate nitrate coordination cannot be made on the basis of infrared data, since the nitrate group has $C_{2v}$ symmetry in each case. However, the assignment of three bidentate nitrate groups is a reasonable one, based upon the bidentate behavior of all three nitrate groups in [La(dipy)$_2$(NO$_3$)$_3$] (dipy = 2,2′-dipyridyl).[11]

The spectra (II, III) for the bis chelates are of two distinct types. The complexes derived from the smaller ions (Sm$^{3+}$–Yb$^{3+}$) show nitrate absorptions corresponding only to $D_{3h}$ nitrate groups. That addition of a second molecule of ligand results in displacement of coordinated nitrate groups is proof that the solid bis chelates contain two molecules of *coordinated* tren.

The spectra of the bis chelates of the larger metal ions (La$^{3+}$–Nd$^{3+}$) show absorptions corresponding to both $C_{2v}$ and $D_{3h}$ nitrate groups. The rather low frequency (1420 cm$^{-1}$) of $\nu_4(C_{2v})$ indicates a small distortion from $D_{3h}$ symmetry and weak coordination.[12] Steric considerations favor a formulation with one coordinated nitrate group. Furthermore, it is unlikely that the small increase in ionic radius occurring from samarium to neodymium (0.03 Å) would allow accommodation of *two* nitrate groups in the coordination sphere.

Anion coordination was observed also in the tetrakis-ethylenediamine chelates. The $\nu_4(C_{2v})$ band for the complexes, formulated as [Ln(en)$_4$NO$_3$](NO$_3$)$_2$, occurs at 1428 cm$^{-1}$,[2a] in agreement with the assignment made in this study. In each series of complexes, the decreasing ionic radius of the lanthanide ions across the lanthanide series results in displacement of the coordinated nitrate group. However, nitrate displacement does not occur at the same metal ion in each system. In the series of ethylenediamine chelates, displacement occurs between samarium and europium, whereas in the series of tren chelates, displacement occurs before samarium. This may be attributed to greater steric crowding in the bis-tren chelates, created by the presence of two additional ethylene groups in the coordination sphere. It is interesting to note that nitrate coordination was not observed in the more sterically hindered *nine*-coordinate tris-diethylenetriamine chelates.

Typical infrared spectra in the NH stretching region are presented in Figure 2. The alterations which occur in this region are accompanied by changes in the nitrate regions of absorption, corresponding to nitrate coordination. The bis chelates (spectrum IV) show a strong absorption at 3260 cm$^{-1}$, which is shifted 30 cm$^{-1}$ toward higher frequency when a nitrate group is introduced into the coordination sphere (spectrum III). A slight splitting of this band is also observed. The effect of nitrate coordination is clearly demonstrated for the mono chelates (spectrum II), in which five well-resolved bands are observed. In each case, however, the stretching frequencies of coordinated NH groups is less than the free-ligand value (spectrum I). This may be attributed to the combined effects of coordination to a positive metal ion[13] and hydrogen bonding between the anion present and the NH proton.[14]

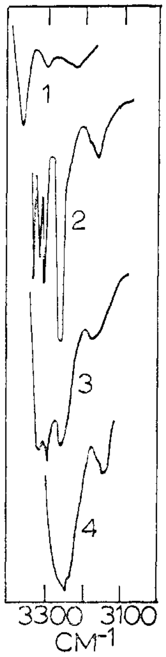

Figure 2.—Infrared spectra of Ln(tren)$_n$(NO$_3$)$_3$ species in the NH stretching region: 1, free tren; 2, Ln(tren)(NO$_3$)$_3$; 3, [Ln(tren)$_2$NO$_3$](NO$_3$)$_2$; 4, [Ln(tren)$_2$](NO$_3$)$_3$.

Similar observations were reported for both the ethylenediamine and 1,2-propanediamine chelates. The large number of NH$_2$ bands observed upon anion coordination may be attributed to nonequivalent sets of amino groups. The increase in frequency of one set may result from repulsions between the nitrogen end of the N–H dipole and the coordinated anion[15] or poorer

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(9) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1945, p 178.

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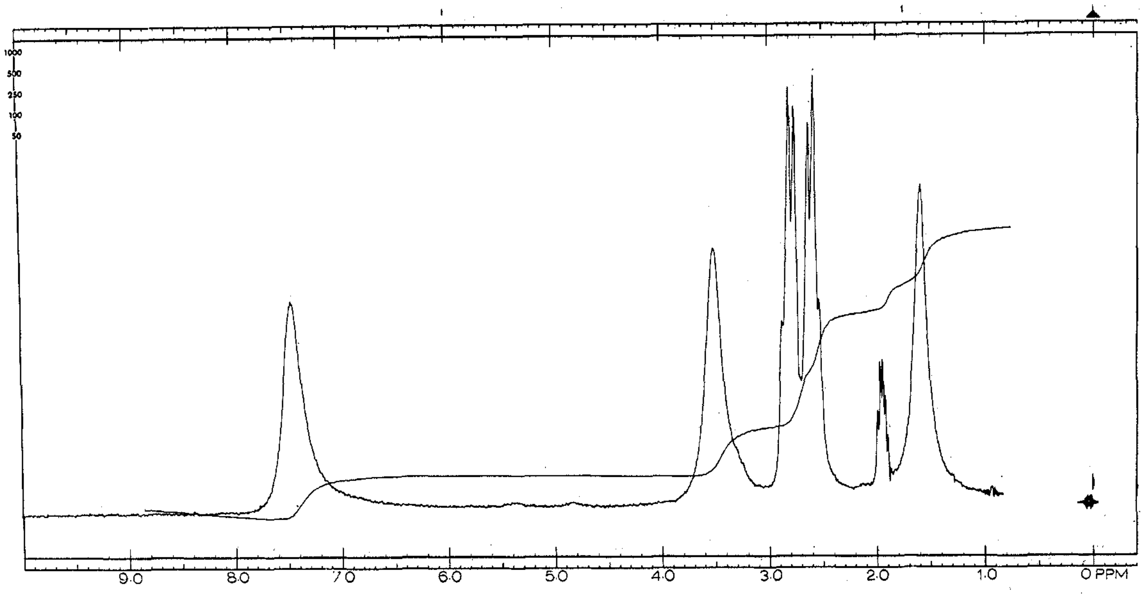

Figure 3.—Nmr spectrum of a deuterated acetonitrile solution containing 0.14 $M$ Nd(tren)$_2$(ClO$_4$)$_3$ and 0.28 $M$ tren.

hydrogen bonding of the amino protons with the coordinated anions.

**Solution Studies.**—The nmr spectrum of a deuterated acetonitrile solution of neodymium perchlorate and excess tren in a 4:1 ligand to metal ion mole ratio is presented in Figure 3. Methylene proton resonances corresponding to both coordinated and free ligand are observed, indicating *slow* intermolecular ligand exchange on the nmr time scale. A complete investigation of the kinetics and mechanism of ligand exchange is currently being carried out.[16] The free-ligand methylene resonance is identified by its characteristic $A_2B_2$ splitting pattern centered at 2.65 ppm and is shifted 0.17 ppm from the resonance position obtained in the absence of the metal ion. The NH$_2$ resonance of the free ligand occurs at 1.54 ppm. The two resonances of equal intensity at 3.48 and 7.41 ppm are assigned to the two magnetically nonequivalent methylene groups of the coordinated ligand. The downfield position of these peaks is a result of a contact and pseudocontact interaction with the paramagnetic metal ion.[17] That only two methylene proton resonances are observed is indicative of rapid intramolecular exchange and/or chelate ring inversion. The NH$_2$ resonance of the coordinated ligand could not be observed, presumably due to effective relaxation by the metal ion. The integrated intensities of the methylene protons of the coordinated and free ligand are equal, thus establishing the existence of the Ln(tren)$_2^{3+}$ species in solution. The quintet observed at 1.90 ppm is assigned to the isotopic solvent impurity CHD$_2$CN. The nmr spectrum was not obtained for nitrate salts of these chelates due to their limited solubility in acetonitrile.

Calorimetric measurements of the total enthalpy of complexation of praseodymium and gadolinium perchlorate in acetonitrile were made to determine the number of nitrogen atoms on each ligand molecule which are involved in coordination. The values obtained ($\Delta H$(Pr) = $-62.5 \pm 1.5$ kcal mol$^{-1}$; $\Delta H$(Gd) = $-60.3 \pm 1.5$ kcal mol$^{-1}$) agree with the enthalpy changes corresponding to the formation of eight metal–nitrogen bonds in the tetrakis-ethylenediamine chelates[5] ($\Delta H$(Pr) = $-59.9$ kcal mol$^{-1}$; $\Delta H$(Gd) = $-60.9$ kcal mol$^{-1}$). For comparison, the enthalpy change corresponding to the formation of six metal–nitrogen bonds in the tris-ethylenediamine chelates is only 47–51 kcal mol$^{-1}$. Since the nitrogen atoms in each of these ligands are expected to be of comparable donor strength, tetradentate coordination by each ligand is indicated.

Conductivity data for acetonitrile solutions containing lanthanide nitrates (0.001 $M$) and various mole ratios of tren are presented in Table III. The nonelectrolytic behavior of lanthanide nitrates in acetonitrile has been noted previously[1,5] The data for the mono chelates also are indicative of nonelectrolytic behavior, consistent with the solid-state formulation [Ln(tren)(NO$_3$)$_3$]. However, the data for the bis chelates, as well as solutions containing excess ligand, are not in the range expected for either 2:1 ([Ln(tren)$_2$NO$_3$](NO$_3$)$_2$) or 3:1 ([Ln(tren)$_2$](NO$_3$)$_3$) electrolytes in acetonitrile (1:1, 175 ohm$^{-1}$ cm$^2$ mol$^{-1}$;[18] 2:1, 285 ohm$^{-1}$ cm$^2$ mol$^{-1}$;[18] 3:1, >400 ohm$^{-1}$ cm$^2$ mol$^{-1}$).[19]

TABLE III

MOLAR CONDUCTIVITIES OF ACETONITRILE SOLUTIONS CONTAINING LANTHANIDE SALTS AND $\beta,\beta',\beta''$-TRIAMINOTRIETHYLAMINE

| Lanthanide salt | $\Lambda_M$(ligand:metal),[a] ohm$^{-1}$ cm$^2$ mol$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | $\Lambda_M$(0:1) | $\Lambda_M$(1:1) | $\Lambda_M$(2:1) | $\Lambda_M$(3:1) | $\Lambda_M$(5:1) | $\Lambda_M$(10:1) |
| La(NO$_3$)$_3$ | 27.4 | 38.6 | 93.2 | 162 | 183 | 196 |
| Pr(NO$_3$)$_3$ | 13.5 | 14.6 | 116 | 163 | 174 | 188 |
| Nd(NO$_3$)$_3$ | 15.1 | 20.7 | 98.3 | 132 | 153 | 177 |
| Sm(NO$_3$)$_3$ | 17.9 | 16.2 | 107 | 147 | 180 | 208 |
| Gd(NO$_3$)$_3$ | 13.8 | 22.2 | 116 | 150 | 170 | 183 |
| Dy(NO$_3$)$_3$ | 10.3 | 23.0 | 121 | 177 | ... | 202 |
| Et(NO$_3$)$_3$ | 6.4 | 21.6 | 119 | 190 | 203 | 207 |
| Yb(NO$_3$)$_3$[b] | 5.3 | 29.6 | 158 | 186 | ... | 203 |
| Nd(ClO$_4$)$_3$[b] | 450 | ... | ... | ... | ... | 475 |

[a] Concentration of Ln(NO$_3$)$_3$ is 0.001 $M$. [b] $\Lambda_M$ measured at infinite dilution.

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[16] M. F. Johnson, Doctoral Dissertation, St. Louis University, work in progress.

[17] E. R. Birnbaum and T. Moeller, *J. Amer. Chem. Soc.*, **91**, 7274 (1969).

[18] J. F. Coetzee and G. P. Cunningham, *ibid.*, **87**, 2529 (1965).

[19] D. A. Durham, G. H. Frost, and F. A. Hart, *J. Inorg. Nucl. Chem.*, **31**, 833 (1969).

The conductivity of a neodymium perchlorate solution is presented for comparative purposes and is typical of a 3:1 electrolyte.

The low conductance values obtained for nitrate solutions containing excess ligand indicate that the equilibrium

$$\mathrm{Ln(tren)(NO_3)_3 + tren \rightleftarrows Ln(tren)_2(NO_3)_n{}^{(3-n)+} + (3-n)NO_3{}^-} \quad (n = 0, 1)$$

lies predominantly to the left. This behavior is attributed to the coordinating ability of the nitrate group, rather than intrinsic instability of the bis chelate. Thus the thermodynamically favored species in solution is the mono chelate containing three coordinated nitrate groups. Similar results were observed in the diethylenetriamine system, in which $\mathrm{Ln(dien)_2(NO_3)_2{}^+}$ was established as the favored species in solution, even though $\mathrm{[Ln(dien)_3](NO_3)_3}$ was isolable from solution in pure form. The isolation of pure bis-tren chelates containing at most one coordinated nitrate group is apparently due to a greater insolubility of the bis chelate in acetonitrile, since nitrate displacement is not favored thermodynamically.

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# Photoreduction of Tris(1,10-phenanthroline)iron(III)

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Tris(1,10-phenanthroline)iron(III) undergoes photoreduction in acidic aqueous media. The effects of acid concentration and added scavengers indicate that water is the electron donor in the photoreaction and that secondary thermal reactions of $\mathrm{Fe(phen)_3{}^{3+}}$ with OH radicals influence apparent overall quantum yields. Despite the presence of an intense ligand→metal charge-transfer band in the visible spectrum of $\mathrm{Fe(phen)_3{}^{3+}}$, the complex undergoes photoreduction only in the ultraviolet. The excited state(s) responsible for the observed photochemistry cannot be conclusively identified on the basis of current understanding of the charge-transfer spectrum of $\mathrm{Fe(phen)_3{}^{3+}}$.

Correlation of redox photochemistry with the locations of charge-transfer excited states (hereafter denoted "CT" states) in coordination compounds is an area of considerable current activity.[1] Although intramolecular CT absorption spectra of metal complexes with 1,10-phenanthroline (subsequently abbreviated "phen") and its relatives have been discussed,[2] photochemistry of phen complexes has received little attention. We have been especially intrigued by a study of photoreduction of $\mathrm{Fe(phen)_3{}^{3+}}$ published by Baxendale and Bridge[3] in 1955. According to their observations, $\mathrm{Fe(phen)_3{}^{3+}}$ undergoes efficient photoreduction to $\mathrm{Fe(phen)_3{}^{2+}}$ only at wavelengths below 300 nm. A spin-allowed $\pi \rightarrow t_2$ CT band[2] appears in the visible region (*ca.* 600 nm), but irradiation in that region effects no photoreduction of $\mathrm{Fe(phen)_3{}^{3+}}$. Unfortunately, these studies were performed in media containing high concentrations of formic acid, which absorbs in the ultraviolet region and is known to undergo photodecomposition in aqueous solution, yielding OH and CHO radicals as primary products.[4] Because it is highly probable that one or both of the photolysis products of formic acid can react thermally with $\mathrm{Fe(phen)_3{}^{3+}}$, the significance of the quantum yield data reported by Baxendale and Bridge for wavelengths below 300 nm is dubious. Accordingly, we have performed an investigation of photoreduction of $\mathrm{Fe(phen)_3{}^{3+}}$ in acidic aqueous media in the absence of extraneous photochemically active solutes.

## Experimental Section

**Materials.**—Tris(1,10-phenanthroline)iron(III) perchlorate was prepared by oxidizing $\mathrm{Fe(phen)_3{}^{2+}}$ with $\mathrm{Cl_2}$ in aqueous solution; the perchlorate salt of $\mathrm{Fe(phen)_3{}^{3+}}$ was then precipitated by addition of sodium perchlorate. The solid was washed with 10 *M* aqueous sulfuric acid until supernatants were free of $\mathrm{Cl^-}$; it was dried and stored *in vacuo* in the dark. An nmr spectrum (60 MHz) of this preparation of $\mathrm{Fe(phen)_3{}^{3+}}$ in concentrated $\mathrm{D_2SO_4}$ agreed well with that published by DeSimone and Drago.[5]

Potassium ferrioxalate[6] and uranyl oxalate[7] for actinometry were prepared and purified by literature procedures. Methyl methacrylate was repeatedly washed with 5% aqueous NaOH to remove inhibitors, washed with distilled water, and then vacuum distilled. The purified material was stored at 4° in the dark in evacuated ampoules until used. Water was distilled twice over alkaline permanganate. Reagent grade $\mathrm{D_2SO_4}$ (Merck Sharp and Dohme of Canada) and $\mathrm{H_2SO_4}$ were used as received.

**Methods.**—Two photochemical irradiation sources were used. In the first, 2537-Å light from a helical low-pressure mercury lamp was impinged upon cylindrical quartz cuvettes in a merry-

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